

## On Debye temperature anomaly observed in Ge-Se-Ag glasses

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### **Abstract:**

Anomalous values of Debye temperature have been obtained from recoil free factor measurements Ge-Se-Ag glasses recently [1]. In the present paper we show that this anomaly may arise due to the presence of anharmonic potential at the high spin ferrous site. We use q Lamb Mossbauer factor and anharmonic Lamb Mossbauer factor to study this anharmonicity

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## Motivation:

Chalcogenide glasses have very interesting microscopic and macroscopic properties. One such example of chalcogenide glasses Ge-Se-Ag systems, has been studied by Arcondo et.al.[1] recently. From Mossbauer spectroscopy measurements of Ge-Se-Ag systems, it is clear that ferrous is present in low spin and high spin states. Low spin  $Fe^{2+}$  corresponds to octahedral co-ordination environment and high spin  $Fe^{2+}$  corresponds to distorted octahedral co-ordination environment. It is also observed that two environments correspond to two Debye temperatures. The Debye temperatures of  $\Theta_D = 290$  K corresponds to high spin  $Fe^{2+}$  state and  $\Theta_D = 370$  K corresponds to low spin  $Fe^{2+}$  sites of Ge-Se samples with  $Ag_{10}$ . These two values of  $\Theta_D$  indicate presence of two phases. The XRD of Ge-Se-Ag glasses shows single or homogeneous phase [1]. The presence of single glass transition also indicates presence of single [1] or homogeneous phase.

In this paper we show that Mossbauer recoil free factor data can also be explained using single value of Debye temperature thereby agreeing with XRD and glass transition results. It is important to note that Mossbauer recoil free factor is very sensitive to the nature of potential. The standard form of Lamb Mossbauer factor (equation 8) has been derived for harmonic potential. We presume that at low spin site of  $Fe^{2+}$  that there is presence of harmonic potential and equation (8) can be applied to calculate Debye temperature. At high spin site of  $Fe^{2+}$ , we assume there is anharmonic potential. The presence of anharmonic potential at high spin site modifies the temperature dependence of normal f-factor, thereby resulting in biased calculation of Debye temperature when we use equation (8) which holds only for harmonic potential. Again it is natural to assume that the presence of anharmonic potential at high spin  $Fe^{2+}$  is due to the distorted octahedral co-ordination environment.

In the following we use deformed Lamb Mossbauer factor and conventional anharmonic Mossbauer recoil free factor to study anomalous nature of  $\Theta_D$  at  $Fe^{2+}$  high spin site.

## Deformed Lamb Mossbauer factor:

Quantum deformation of algebras and groups have resulted in deformed analogue or commonly known as q analogue of harmonic oscillator. Statistical properties of q Bose gas has been studied in detail [2,3] and has found wide range applications in nuclear physics, molecular physics, non linear optics and condensed matter physics [4] and references therein. It has been observed that eigen values of q-harmonic oscillators are not equally spaced. The spectrum of q harmonic oscillator has been found to be similar to the spectrum of anharmonic oscillator [5,6]. Atroni et. al. [7] have interpreted the physical significance of q parameter as a measure of degree of anharmonicity. It has been found that parameter q in q specific heat [8] is a measure of degree of anharmonicity. It

has been argued that specific heat measurements in superfluids can be explained only if phonons follow q deformation algebra. So by studying q version of Lamb Mossbauer factor it has been possible to study anharmonicity in q f-factor[9].

The Hamiltonian of q harmonic oscillator is defined by

$$H = \frac{1}{2}\hbar\omega(a^+a + aa^+) \quad (1)$$

where  $a^+$  and  $a$  are creation and Annihilation q-Bose Operators which satisfy the following commutation relation

$$aa^+ - qa^+a = 1 \quad (2)$$

q is deformation index and

$$a^+a = [N] \quad (3)$$

is number operator. The square bracket is a q-number. For any number r, the q number defined as

$$[r] = \frac{q^r - \frac{1}{q^r}}{q - \frac{1}{q}} \quad (4)$$

Average occupation Number

$$n_q = \frac{\sum_0^\infty T \exp(-T)}{\sum_0^\infty \exp(-T)} \quad (5)$$

where

$$T = \frac{1}{2}([n+1] + [n] - 1) \quad (6)$$

The Lamb Mossbauer Factor using equations generalized quantum mechanics

$$\log f_0 = \frac{-E_\gamma^2}{3mc^2} \int_0^{\omega_{max}} \left(\frac{1}{2} + n_q\right) \left(\frac{\hbar}{k}\right)^3 \frac{\omega_i^2 d\omega_i}{\Theta_D^3 \hbar \omega_i} \quad (7)$$

where  $x = \frac{\hbar\omega}{kT}$  and  $\hbar\omega_{max} = k\Theta_D$ . The equation(7) holds for real and positive value of q. It has been shown that for deformed Lamb Mossbauer factor parameter q decides the nature of f-factor (in equation 7) dependence on temperature. Deformed Lamb Mossbauer factor has been used to study anharmonicity [9] in antimony, prussian blue analogues. It has also been used to study anharmonicity in superconductors like  $Nb_3Sn$  [10] and  $YBaCuO$  [11].

In the limit of  $q \rightarrow 1$ , equation (7) reduces to

$$\log f_0 = \frac{-3E_\gamma^2}{mc^2\Theta_D} \left[ \frac{1}{4} + \left(\frac{T}{\Theta_D}\right)^2 \int_0^{\frac{\Theta_D}{T}} \frac{x dx}{e^x - 1} \right] \quad (8)$$

This is well known expression for Lamb Mossbauer factor using normal quantum mechanics.

**Conventional anharmonic approach:**

Marradudin and Flinn have derived a relationship which describes the effect of anharmonicity on the recoil free factor  $f$ . This relationship is given as [12,13]

$$\ln f = \frac{-6RT}{\Theta_D^2}(1 + \epsilon T + \dots) \quad (9)$$

In above equation,  $R$  is the recoil energy of nucleus,  $\epsilon$  is the anharmonic coefficient. For  $^{57}\text{Fe}$  nucleus,  $R = 22.6$  K. The anharmonic coefficient  $\epsilon$  can be theoretically calculated by using Marradudin and Flinn theory. Experimentally  $\epsilon$  can be measured from recoil free factor versus temperature curves.

The similarity between  $q$  Lamb Mossbauer factor and conventional anharmonic approach has been very well studied in [11,10]. At low temperatures this similarity is not good but above a 'particular temperature' this similarity improves sharply. The value of this 'particular temperature' is strongly dependent on the value of the Debye temperature. For low Debye temperature, the similarity begins at lower temperature [11].

### Discussion and results:

The relationship between normal recoil free factor and Debye temperature is very interesting at all temperatures [14]. For high Debye temperature,  $f$ -factor falls slowly with the increase of temperature. For small Debye temperature  $f$ -factor falls sharply even with small increase of temperature. Lamb Mossbauer factor reduces sharply even at 0 K [14] for a solid with low Debye temperature.

Earlier we have shown that both deformed Lamb Mossbauer and anharmonic Lamb Mossbauer factor affect recoil free factor's dependence on temperature very strongly. It is clear that both  $q$  and  $\epsilon$  affect  $f$ -factor in almost similar manner i.e. larger the value of  $q$  or  $\epsilon$ , larger is their effect on  $f$ -factor and vice versa. Again it is important to note that value of  $\epsilon$  needed to affect the change in  $f$ -factor depends on value of Debye temperature i.e. larger the value of Debye temperature, larger is the value of  $\epsilon$  needed to affect the nature of  $f$ -factor and vice versa. This is also true of  $q$  parameter [10,11]. Thus anharmonic coefficient  $\epsilon$  shares a similar relationship with Debye temperature as deformed parameter  $q$  does. We have shown it earlier that there is a qualitative (if not quantitative) similarity in nature of  $q$  and  $\epsilon$ . Both  $q$  and  $\epsilon$  represent anharmonicity and anharmonicity affects recoil free factor by decreasing it more rapidly than in the case of a normal Debye solid.

Figure 1 depicts four curves (a-d). The curve 'a' corresponds to Debye temperature of  $\Theta_D = 370$  K and curve 'b' corresponds to  $\Theta_D = 290$  K. Both curves 'a' and 'b' have been obtained using normal Lamb Mossbauer factor model of equation(8). Curves 'c' and 'd' has been obtained by using  $q$ -Lamb Mossbauer factor of equation (7). Curves 'c' and 'd' have been obtained for Debye

temperature  $\Theta_D=370$  K. For curve 'c'  $q=1.98$  and for curve 'd'  $q=2.04$ . It is clear that curves 'c' and 'd' obtained for  $\Theta_D=370$  K surround curve 'b' which has been obtained for  $\Theta_D=290$  K. Curve 'b' represents f-factor of high spin  $Fe^{2+}$  site. Curve 'b' is also very similar to curves 'c' and 'd' (for  $T > 100K$ ) which correspond to Debye temperature of  $\Theta_D=370$ .

Figure '2' depicts four curves (a-d). The curve 'a' corresponds to Debye temperature of  $\Theta_D=370$  K and curve 'b' corresponds to  $\Theta_D=290$  K. Both curves 'a' and 'b' have been obtained using normal Lamb Mossbauer factor model of equation(8). Curves 'c' and 'd' have been obtained using conventional anharmonic approach of equation (9). Curves 'c' and 'd' have been obtained for Debye temperature  $\Theta_D=370$  K. For curve 'c'  $\epsilon=0.0031$  and for curve 'd'  $\epsilon=0.0045$ . It is clear that curves 'c' and 'd' obtained for  $\Theta_D=370$  K surround curve 'b' which has been obtained for  $\Theta_D=290$  K. Curve 'b' represents f-factor of high spin  $Fe^{2+}$  site. Curve 'b' is also very similar to curves 'c' and 'd' (for  $T > 100K$ ) which correspond to Debye temperature of  $\Theta_D=370$ .

Curve 'a' in figures 1 and 2, corresponds to Debye temperature  $\Theta_D=370K$ , representing f-factor of low spin  $Fe^{2+}$  site. At low spin site of  $Fe^{2+}$  there is presence of harmonic potential for which  $q=1$  or  $\epsilon=0$ . Thus we can say Curve 'b' in figures 1 and 2, representing f-factor of high spin  $Fe^{2+}$  site, also corresponds to Debye temperature  $\Theta_D=370$  K for which there is presence of anharmonic potential corresponding to  $q=2.02 \pm 0.03$  or  $\epsilon=0.0038 \pm 0.0007$ . Thus curve 'b' is indeed a case of anharmonic behaviour because  $\epsilon \neq 0$  or  $q \neq 1$  and curve 'a' is a case of harmonic behaviour because  $\epsilon=0$ , or  $q=1$ . However, in the same lattice one site cannot experience harmonic behaviour ( i.e.  $q=1$ , or  $\epsilon=0$ ) and another site cannot experience anharmonic behaviour ( i.e.  $q \neq 1$  or  $\epsilon \neq 0$ ) for similar thermal conditions. So Ge-Se-Ag glasses do not experience whole lattice anharmonicity. The present problem is not a case of anharmonicity due to thermal expansion but a localized effect due to the presence of anharmonic potential well in the vicinity of high spin  $Fe^{2+}$  due to the presence distorted octahedral co-ordination environment. The distorted octahedral co-ordination environment may create anharmonic potential at high spin site, modifying the f-factor, thereby resulting in biased calculation of different Debye temperature using standard Lamb Mossbauer factor. In the present studies the value of  $q=2.02$  or  $\epsilon=0.0038$  may be quantifying the anharmonicity due to the presence of this potential well. Almost a similar scenario has been observed in high temperature properties of YBaCuO superconductors [11].

Anharmonicity in Mossbauer spectroscopy is either a high temperature or low temperature phenomena. High temperature anharmonicity in Lamb Mossbauer occurs when small to moderate deviations take place in the parabolic nature of potential. These deviations exist in only high temperature region. In contrast to this low temperature anharmonicity arises due to presence

of non-parabolic potential and will be appreciably present as anharmonic term even at absolute zero temperature. Recoil free factor is the product [15] of harmonic and anharmonic terms. The harmonic term is subject to linear temperature dependence while the anharmonic terms exhibits little or no temperature dependence. Therefore the effect of low temperature anharmonicity is to displace the harmonic curve by large values at all temperatures. It may be interesting to study f-factor dependence of Ge-Se-Ag glasses in low temperature region to establish true nature of anharmonicity.

**Conclusions:** In this paper we have shown that Debye temperature anomaly observed in Ge-Se-Ag glasses can be solved by assuming presence of the anharmonic potential at the high spin ferrous site. This anharmonic potential at ferrous site may arise due to the distorted octahedral co-ordination environment.

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### Figure captions

Figure 1: Temperature dependence of Lamb Mossbauer factor and q Lamb Mossbauer factor for various values of Debye temperature. The curves 'a' and 'b' have been obtained using equation (8) and curves 'c' and 'd' have been obtained using equation (7).

Figure 2: Temperature dependence of Lamb Mossbauer factor and anharmonic Lamb Mossbauer factor for various values of Debye temperature. The curves 'a' and 'b' have been using equation (8) and curves 'c' and 'd' have been obtained using equation (9).

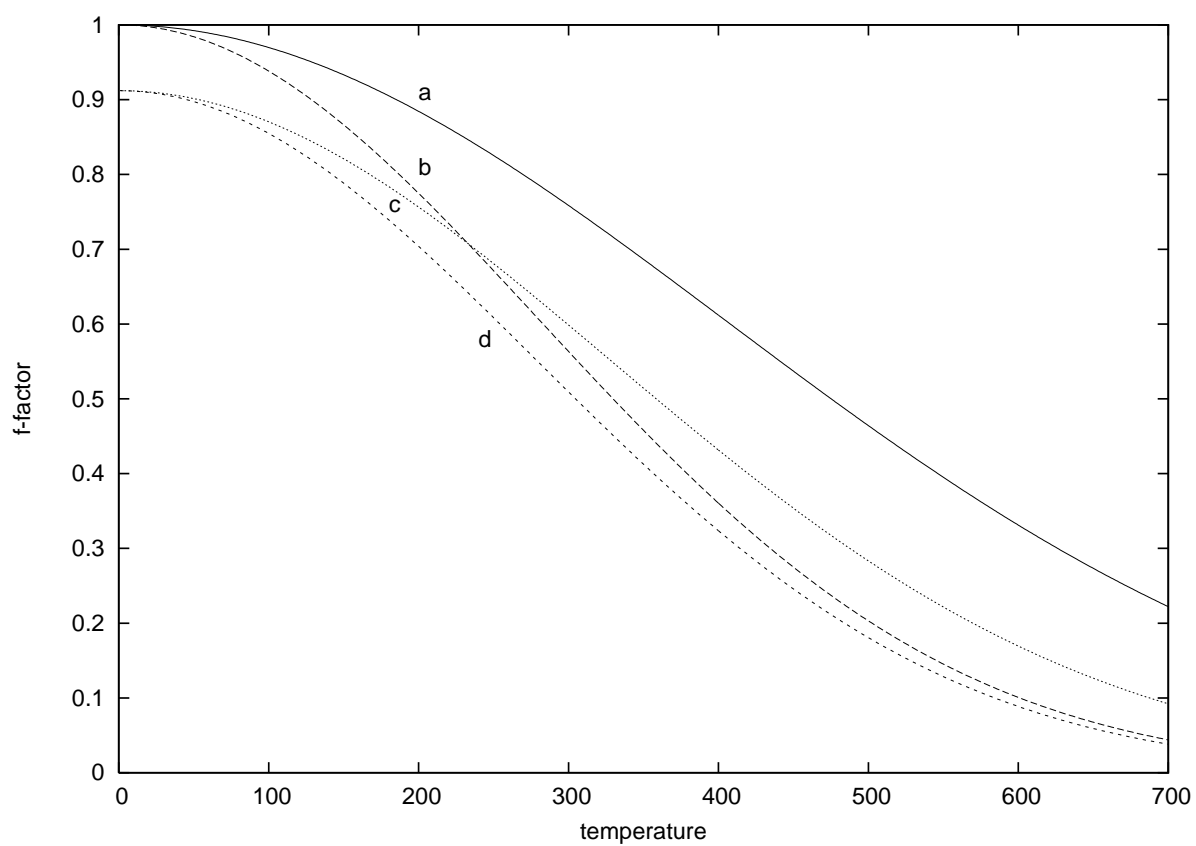


Figure 1:



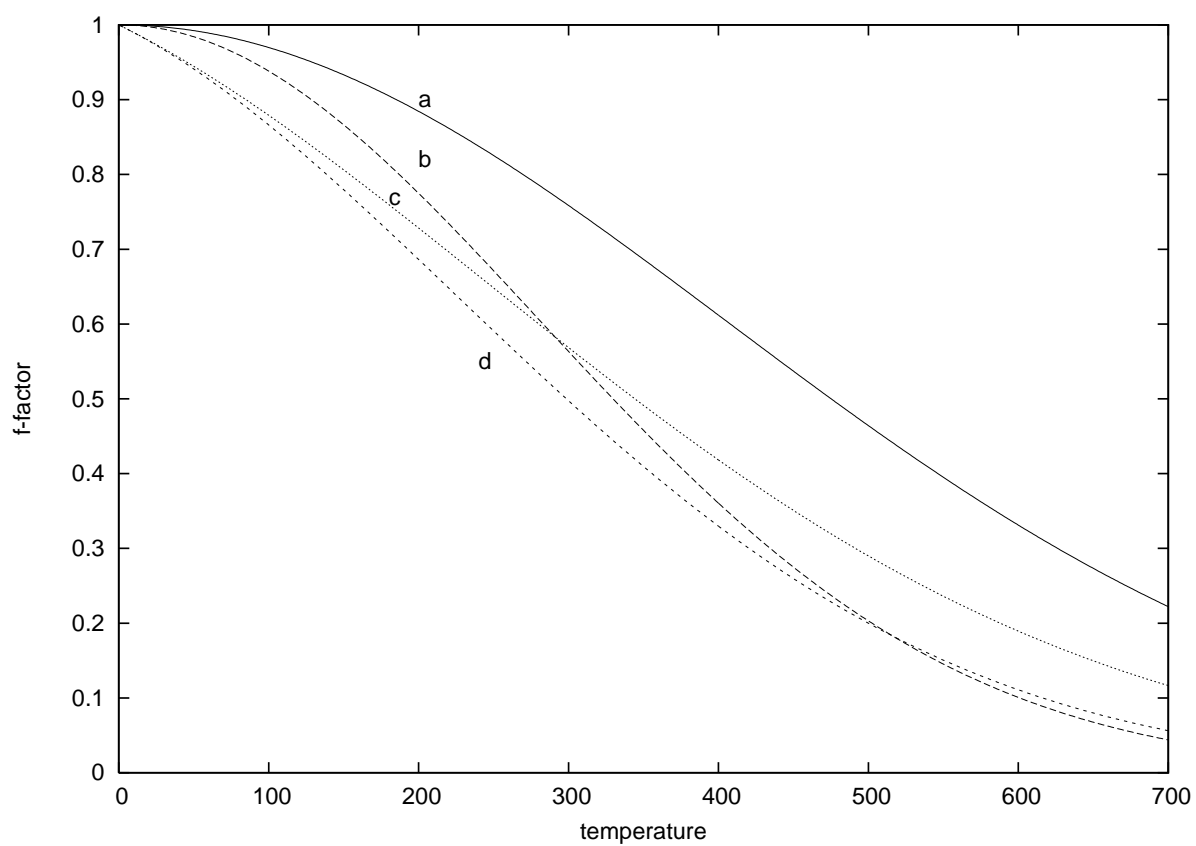


Figure 2: